ACTIVITY REPORT

October 2000

Natural Gas & Oil Technology Partnership

bringing department of energy national laboratories capabilities to the petroleum industry

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Note: Natural Gas and Oil Technology Partnership projects are reported according to the following schedule:

January, March, May, July, September, November	**February, April, June, August, October, December**
Oil and Gas Recovery Technology Drilling, Completion, and Stimulation Technology Diagnostic and Imaging Technology	Upstream Environmental Technology Downstream Environmental Technology

Natural Gas and Oil Technology Partnership on the World Wide Web: http://www.sandia.gov/ngotp/

Upstream Environmental Technology

Continuous Monitoring of Particulate Matter and Particulate Matter Precursor Emissions from Stationary Sources (Chevron and SNL)

Project is in close-out phase.

Development of an In-Well Oil/Water Separator for *In Situ* Recycling of Produced Water (Baker Hughes, Chevron, CINC, Oak Ridge Tool & Engineering, Phillips, REDA Pump, Texaco, Unocal, and ORNL)

Highlights:

- System operated on solids/water/oil feed stream.
- Placed contract for manufacture of redesigned housing for centrifugal separator.

Bench-scale testing continues using a model V-2 (2-in. rotor) centrifugal separator from CINC, Inc., and synthetic oil.

Solids/water/oil were separated using a hydrocyclone in combination with the centrifugal separator. The feed stream contained 3% sand, 47% sea water, and 50% synthetic oil. The system worked very well producing a clean split of oil and water in the separator when the solids had been removed in the hydrocyclone.

The housing for the separator was redesigned and will be machined in plexiglass. The new housing will accept a longer rotor, which will allow for increased throughput capacity. The portion of the rotor housing that directs the exit of the separated streams was also redesigned not to protrude from the sides, but to run down the side. Also, exchangeable parts for the internal parts of the housing were designed to allow for adjustment of the collection well volumes. A contract was placed for manufacture of the redesigned housing.

Stationary Source Emission Control Using Plasma-Assisted Catalysis (Cummins Engine, Edison Chouest Offshore, and LLNL)

Project is in close-out phase.

Reducing Chemical Use and Toxicity in Produced-Water Systems (BP Amoco, Rhorback Casasco Systems, and ANL)

Highlights:

- Improved electrode design tested for reproducibility in a microbially influenced corrosion test system.
- Software prototype completed.

A corrosion experiment (ECN36) using ANL's surface-modified electrode was completed, and the results were analyzed. ECN36 was run to demonstrate the increase in sensitivity to sustained localized pitting (SLP) corrosion on electrochemical noise (ECN) probes by using surface-modified electrodes (SME) in a microbially influenced corrosion (MIC) environment. In the experiment, a simulated produced-water solution in the flow loop test system was inoculated with sulfate-reducing bacteria and acid-producing bacteria that are responsible for initiating MIC. Two flow loops were used. Each loop included one original ECN probe and one newly designed ECN probe. The new ECN probe consists of one SME and one non-surface-modified electrode (NSME). The original ECN probe includes two NSMEs. The two SMEs developed severe localized pitting corrosion. The maximum pitting corrosion rate (measured by using an optical microscope) on these SMEs was four to seven times higher than the general or uniform corrosion rate (measured by weight loss). None of the NSMEs developed significant localized pitting corrosion. Only uniform pitting corrosion, where small pits are uniformly seen all over the electrodes surface, was observed. The uniform pitting corrosion rates in these NSMEs were much smaller than their general corrosion rates. Another experiment (ECN37) is planned to verify the linear proportionality between the general corrosion rates

of the NSMEs in the new ECN probes and the total noise current. The optimal conditions of the surface roughness of the SME will also be determined in the next experiment using the MIC environment system.

The prototype of a "user friendly" software package for automatic measurement and data interpretation with the corrosion monitoring system was completed. This prototype software was written using the industrial standard data acquisition program platform, LabVIEW, from National Instrument, Inc. Using the new software, the corrosion status of the equipment can be monitored online and displayed and updated every 5–10 minutes. The information that is displayed includes the corrosion mechanism (i.e., sustained local-zed vs. uniform corrosion), the corrosion current, and estimated uniform corrosion rate. Laboratory testing of the new software is being conducted. The software is also being modified to include monitoring of multiple ECN sensors.

Sulfide Removal in Produced Brines by Microbial Oxidation

(Phillips, U of Tulsa, and INEEL)

Highlights:

- Completed conceptual-scale design.
- Continued investigation of the stoichiometry for nitrate reduction.
- Evaluated changes in population dynamics.
- Determined that culture conditions (temperature, pH) can significantly improve the specific activity of the Coleville enrichment for sulfide oxidation.
- Investigated an immobilization strategy for the Coleville enrichment culture.

Experiments from the evaluation of alternate sulfur compounds resulted in two unique metabolic observations:

1. Coleville organism (CVO) (*Thiomicrospira* sp. strain CVO) appears to form an inclusion complex when grown on a specific polysulfide complex—evident in direct microscopic evaluations of DAPI (4',6-Diamidino-2-phenylindole dihydrochloride hydrate) stained cells.
2. The counter ion of the polysulfide complex potentially affords a protective mechanism that results in more robust biomass.

Experiments to evaluate the potential protective qualities of the counter ion and the polysulfide complex are ongoing. Titration experiments to determine the maximum concentration of polysulfides tolerable by the cells are nearing completion.

Evaluation of additional sulfide-oxidizing organisms began in October. Results will be directly compared to CVO and used in the selection process to support field application. These evaluations were initiated to enable direct comparison with microbial efficacy for application.

A cooperative research and development agreement meeting was held October 18 in Idaho Falls, ID. Technical principals from Phillips Petroleum and the University of Tulsa attended.

A contract extension with Dr. Kerry Sublette, of the University of Tulsa, was completed. The extension allows a transition into the new fiscal year without interruption of work.

Characterization of Soluble Organics in Petroleum Waste Water

(BP Amoco, Chevron, Marathon, Phillips, Shell, Statoil, and ORNL)

The objective of this project is to characterize and evaluate water solubles aimed at reducing future production of these contaminants in produced water. Quantitative characterization data are being acquired as the first step in this activity. ORNL is currently identifying water soluble organics in produced water derived from Gulf of Mexico (GOM) crude oil/brine contacts. Thus far, 13 oil/brine simulant contact experiments have been performed. These include varying the percent water/oil cut (80–20%), pH (4.7–9.0), salinity (45,000–110,000 ppm chloride) and temperature (25–75°C) of the brine simulant. A pressure vessel has been designed and will be fabricated as soon as the purchase requisition is in place. This equipment will be used to determine the effect of pressure on water/oil mixtures as the final experimental variable.

The primary classes of organic compound being identified in produced water samples include total extractable material (TEM) by methylene chloride

solvent extraction, hexane-extractable material (HEX), total saturated hydrocarbons (TSAT), total aromatic hydrocarbons (TARO), and total polar hydrocarbons (TPOL). Gas chromatographic/flame ionization detection also provides carbon size (C_6–C_{10}, C_{10}–C_{20}, C_{20}–C_{28}) characterization within each of these chemical classifications.

Both the neat GOM crude oil and produced water samples have been analyzed using the characterization scheme above. Results for the analysis of neat oil suggest that the hydrocarbon content for the C_{20}–C_{28} range is about 700 g/kg. All oil components are extractable in methylene chloride; 55% of carbon mass occurs in the C_6–C_{10} range and 44% in the C_{10}–C_{20} range. A majority of the light carbon material in the oil is lost through evaporation at 55°C as the methylene solvent is exchanged for hexane. Saturated hydrocarbons make up approximately 80% of the $C_{1-0}C_{20}$ carbon range in the HEX fraction; aromatic and polar compounds make up the remaining constituents.

Methylene chloride-extractable material in the equilibrated produced water is typically present at 20–30 ppm. There is a slight negative trend in the water soluble organic (WSO) content of the TEM fraction as the water cut increases. Analytical results obtained in the characterization of crude oil will be used to determine approximate distribution coefficients of chemical as a function of oil/brine volumes. Chemical fractionation of TEM content suggests that 80–90% of WSO is present as polar compounds; the next largest fraction is that of aromatic materials. The visibly colored material is present in the polar fraction. The chemical character of the water soluble material does not vary with water cut. The variation in TEM appears to be due to the relative solubility of the C_{10}–C_{20} carbon range material.

The WSO content increases with pH, primarily due to the enhanced solubility of the polar organic compounds. Again, there appears to be an enhanced solubility of the C_{10}–C_{20} carbon range material with pH. Variation of salinity or temperature does not significantly alter WSO content. However, in the case of variations in brine temperature, the net WSO content is the result of reduced $C_{6-}C_{10}$ material and increased C_{10}–C_{20} content with increased temperature. Remaining testing with this particular source of crude oil includes a final pH study and a series of pressure studies.

Ecological Framework to Evaluate the Effect of Size and Distribution of Releases at Upstream Petroleum Sites

(American Petroleum Institute, BP Amoco, Chevron, Exxon, Gas Technology Institute, Texaco, Unocal, LBNL, ORNL, and LLNL)

Highlight:

- Work presented at PERF meeting.

LLNL and ORNL attended a Petroleum Environmental Research Forum (PERF-99-01) meeting hosted by Chevron in Richmond, CA, October 24–25. Project researchers presented work completed on the Tall Grass Prairie Preserve study site and discussed future work. The presentation was well received, and the oil industry representatives endorsed the direction of the project.

LLNL completed a draft Geographic Information Systems (GIS) data collection protocol and will provide it to ORNL for input. LLNL will incorporate the oil industry's request to list the minimum data layers necessary to allow landscape analysis of exploration and production (E&P) sites. ORNL continues to work on obtaining additional data layers for the Tall Grass Prairie site, including Airborne Visible Infrared Imaging Spectrometer multispectral data and Landsat data. LLNL continues to work on the GIS site development and is finalizing hardware specifications for the host site. ORNL is working on a draft summary of the literature review on population viability analysis. LLNL continues work on a literature review, which includes approximately 300 papers, on critical habitat size, fragmentation and modeling. ORNL completed an initial analysis of vegetation types in which most E&P facilities in the U.S. are found.

Estimation and Reduction of Air Quality Modeling Uncertainties (Envair, EPRI, and LBNL)

New FY00 project: Reporting will start three months after the DOE FY00 funding arrives at the laboratories.

Downstream Environmental Technology

Bioprocessing of High-Sulfur Crudes via Application of Critical Fluid Biocatalysts (Texaco, UOP, and INEEL)

Experiments focused on polyethylene glycol (PEG) - cytochrome c (CYT c) conjugate, supplied by ORNL, and biocatalyst immobilization using a UOP support material. Dibenzothiophene and thioanisole were explored as model organic-sulfur compounds.

Studies using the PEG-CYT c conjugate showed that no measurable transformations of dibenzothiophene took place in toluene solvents. However, transformations of thioanisole to its sulfoxide products were observed using the PEG-CYT c conjugate biocatalyst. Very slight conversion of thioanisole to the sulfoxide products occurred in a liquid benzene solvent, but transformation was evident in supercritical solvents. Carbon dioxide (CO_2), ethane, and trifluoromethane were explored as supercritical fluids. Reaction pressures ranged from 2,000–2,300 psi at a temperature of 40°C. No transformation was observed in supercritical ethane. Slight levels were observed in supercritical CO_2, but transformation was clearly evident in supercritical trifluoromethane.

Support material, supplied by UOP, was used in protein immobilization studies. Proteins investigated included horseradish peroxidase, CYT c, and hemoglobin. Liquid phase studies were conducted in an aqueous buffer, benzene, and toluene. Dibenzothiophene transformation in toluene was not observed. However, thioanisole conversion was measured in both the aqueous buffer and benzene solvent. Support hydration experiments provided negative results for both dibenzothiophene and thioanisole transformations.

An understanding was reached on cooperative research and development agreement issues between the INEEL and UOP and between the INEEL and Texaco. The final documents await approval.

Biological Upgrading of Heavy Oils for Viscosity Reduction (BP Amoco, Chevron, EPRI Chemicals, Natural Gas Center, Texaco, and LBNL)

Results from the first 17 months of the project and the proposed effort for the coming year were presented to the Downstream Industry Panel in Houston, TX, October 11. LBNL found a broad diversity among alkane-oxidizing biocatalysts and that these results have far-reaching impacts on commercial development of bioprocessing systems. FY01 plans include expanding the project to include genetic characterization of the biocatalysts and beginning to isolate thermophilic alkane-oxidizers.

Kinetics of Biochemical Upgrading of Petroleum (Biocat, Chevron, Shell, and BNL)

Report not received.

Enzymatic Upgrading of Heavy Crudes via Partial Oxidation or Conversion of PAHs

(Chevron, Phillips, Texaco, ORNL, and INEEL)

Highlight:

- Agreement signed between ORNL, Texaco, Phillips, and Chevron.

ORNL previously reported development of a *Pichia pastoris* strain engineered for expression of extracellular lignin peroxidase enzyme (LiP). The activity and the amount of enzyme secreted into the medium was, however, lower than the amounts of native enzyme synthesized by *Phaenerocheate chrysosporium*. We therefore conducted DNA sequencing of the cloned gene and have confirmed that the lignin peroxidase gene (*lip*) was inserted in correct orientation and in a correct reading frame into the plasmid used to transform the yeast. We investigated various optimization methods to improve recombinant enzyme production such as optimization of the fermentation conditions as well as media composition; however, the success has been marginal. Further work to improve enzyme production is being focussed on the use of error-prone polymerase chain reaction (PCR) to introduce point mutations in the *lip* gene. The PCR products are cloned into a pCR2.1 plasmid and transformed into TOP10 *E. coli* strain using the original TA cloning kit (Invitrogen, Carlsbad, CA). Plasmid DNA is isolated from the pool of recombinants, and then the pool of mutated genes is excised and subcloned into an appropriate vector for expression in the yeast. These steps are followed by transformation of the plasmids carrying mutated gene copies into the yeast (and also into *E. coli* DH5a to maintain the plasmid for a long term). Once the *Pichia* clones are ready, the recombinant strains will be screened for LiP activity using previously reported protocols.

In the second part of the project, a detailed thermodynamic analysis of the enzymatic reaction for pyrene conversion by cytochrome c biocatalyst was conducted. The analysis is being submitted for publication.

The effort on the entire project is currently reduced because FY 2001 funds are not yet available.

All participants signed the cooperative research and development agreement (CRADA). The agreement has been in effect since October 24. Research progress and plans for future work were presented at a DOE Proposal Review meeting in Houston, TX, on October 12. Separate meetings were also held with the industry participants and INEEL to discuss collaborative activities. In the ongoing collaboration with INEEL, the modified biocatalyst prepared by ORNL was tested by INEEL and reported to be functional in an organic solvent under supercritical conditions. In a discussion with the industry participants about future tasks, it was decided that ORNL will continue its efforts in directed evolution of LiP. The industry participants will be investigating the availability of in-house techniques to do structural analysis of the previously modified enzymes in order to study the structure-function relationships. ExxonMobil has expressed an interest in joining this project. Because the CRADA agreement has already been signed, we are requesting input from existing participants to determine the feasibility of accepting a new participant.

A Predictive Model of Indoor Concentrations of Outdoor $PM_{2.5}$ in Homes

(Aerosol Dynamics, Envair, Western States Petroleum Association, and LBNL)

Indoor and outdoor measurements of particles and gases were conducted during the very successful autumn field campaign in Fresno, CA. Particles were classified with respect to size and composition. Preliminary analysis of NH_4NO_3 particles indicates that outdoor concentrations measured at the experimental house track those measured at First Street, the supersite location. Indoor concentrations of NH_4NO_3 particles are significantly less that outdoor values. LBNL researchers hypothesize that this is because of the deposition of nitric acid (HNO_3) from the gas phase onto surfaces in the indoor environment,

thereby reducing the concentration of HNO_3 in the gas phase. This process occurs because HNO_3 is a very "sticky" molecule, the surface-to-volume ratio is much larger indoors than outdoors, and the deposition of HNO_3 is very facile. Deposition reduces the gas-phase HNO_3 concentration, and this reduction drives the reaction of HNO_3 and ammonia (NH_3):

$$HNO_3\,(g) + NH_3\,(g) <-> NH_4NO_3\,(a)$$

where (g) indicates gas and (a) indicates aerosol, toward the left in an attempt to establish equilibrium.

The current effort is devoted to data analysis and planning the winter field intensive.

Real-Time Characterization of Metals in Gas and Aerosol Phases (BP Amoco, Equilon, Marathon, Phillips, Shell, Eastman Chemicals, and ORNL)

The objectives of this project are to develop and field test a high-precision field portable instrument for real-time measurement of elemental composition in gas and airborne particulate matter in source emissions. DOE had approved the cooperative research and development agreement with the Eastman Chemical Company in September. The instrument is being prepared for the field experiment scheduled for December 2000. The principal investigator participated in the proposal renewal session at Houston, TX, and the Air Research Meeting at Tulsa, OK, in October, which were both sponsored by the NGOTP office. Also in October, we presented a paper on the instrument to the NARSTO science meeting for Fine Particles Research held in Querétaro, Mexico. The meeting was sponsored by several organizations and agencies from Mexico, Canada, and the United States, including DOE and the American Petroleum Institute.

Partnership Office

The Department of Energy's (DOE's) Offshore Technology Roadmap (OSTR) will be rolled out at three regional events in Galveston, TX (November 27); New Orleans, LA (November 28); and Washington, DC (December 5). This roadmap, which is the first step toward increasing oil and gas production from ultra deepwater Gulf of Mexico, is the result of workshops held across the country during July and August. Participants in these workshop included representatives from the production companies, investors, technology and service suppliers, federal and state governments, and non-governmental agencies.

The Partnership wishes to support this DOE effort as part of our goals to provide and transfer the technology from the national laboratories to the domestic oil and gas industry in order to increase critical and strategic production. The Partnership will seek ways in conjunction with DOE Fossil Energy to showcase Partnership technologies that apply to deepwater exploration and production. Included in this approach to evolve the Partnership will be a review of best practices for transfer of national laboratory technology to industry.